

Chemistry and Toxicity of Flame Retardants for Plastics

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An overview of commercially used flame retardants is given. The most used flame retardants are illustrated and the seven major markets, which use 96% of all flame-retarded polymers, are described. Annual flame retardant growth rate for each major market is also projected. Toxicity data are reviewed on only those compositions that are considered commercially significant today. This includes 18 compounds or families of compounds and four inherently flame-retarded polymers. Toxicological studies of flame retardants for most synthetic materials are of recent origin and only a few of the compounds have been evaluated in any great detail. Considerable toxicological problems may exist in the manufacturing of some flame retardants, their by-products, and possible decomposition products.

Introduction

Practically all commercial plastics are "compounded" with various additives to improve their processing and end-use performance. In the order of total volume of additives used in 1974, flame retardants occupied second place after plasticizers with a volume of 384 million pounds (see Table 1) (1).

Table 1. Additives in plastics.

	Amounts $\times 10^{-6}$, lb
Plasticizers	1,650
Flame retardants	384
Colorants	311
Heat stabilizers	92
Lubricants	67
Antioxidants	30
Organic peroxides	26
Blowing agents	14
Antistats	4
Ultraviolet stabilizers	4

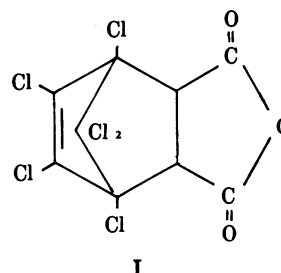
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Types of Flame Retardants

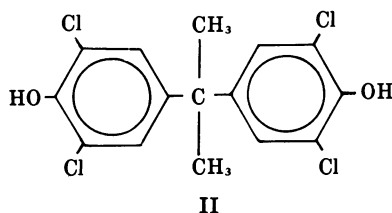
The major basic chemical elements in most commercial flame retardants are chlorine, phosphorus, and bromine. Most flame retardants contain one or more of these elements, often in addition to such other elements as nitrogen and antimony. The presence of nitrogen and/or antimony enhances the effectiveness of the basic elements in certain combinations (formulations).

Chlorine-Containing Flame Retardants. Chlorine-containing flame retardants are of three chemical types: aliphatic, cycloaliphatic, and aromatic (2). Chlorinated paraffins are by far the most widely used aliphatic chlorine-containing flame retardants. These low cost products are offered in a broad range of chlorine content and physical properties. Cycloaliphatic chlorine-containing flame retardants are best represented by Diels-Alder adducts of hexachlorocyclopentadiene. The best known example in this class is chlorendic anhydride (I).



This flame retardant is used as an intermediate in the production of flame-retarded epoxy resins and unsaturated polyesters.

Of the various aromatic chlorocompounds, the best known commercial flame retardants are tetrachlorophthalic anhydride, chlorinated naphthalenes, and tetrachlorobisphenol A (II).



Phosphorus-Containing Flame Retardants.

The best known commercial phosphorus-containing flame retardants are phosphate esters: tricresyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tris(isopropylphenyl) phosphate, and tris(2-ethylhexyl) phosphate (2).

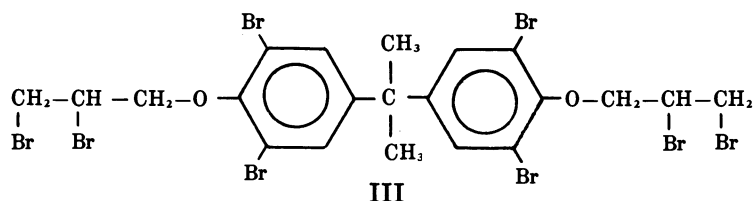
Bromine-Containing Flame Retardants.

Bromine-containing flame retardants can be divided into four major types: aliphatic, cycloaliphatic, aromatic, and ionic (2). In general, bromine-containing flame retardants represent the most diverse chemical structural types of all flame retardants. Some better known examples of aliphatic bromine-containing flame retardants are: poly(vinyl bromide), 2,3-dibromopropanol, dibromoneopentyl glycol, tribromoneopentyl alcohol, and dibromobutenediol.

An example of cycloaliphatic bromine-containing flame retardants used commercially is hexabromocyclododecane. More examples of this type of flame retardants are used; however, they are proprietary compounds and their structures are not known.

The most widely used aromatic bromine flame retardant is decabromodiphenyl ether. Other well-known examples are hexabromobenzene, hexabromobiphenyl, decabromobiphenyl, and tetrabromophthalic anhydride.

A flame retardant containing both aliphatic and aromatic bromine is bis(3,3-dibromopropyl ether) of tetrabromobisphenol A (III):



This flame retardant has generated significant commercial interest in Europe for use in polyolefins.

Flame retardants containing ionic bromine include ammonium bromide and various phosphonium bromides.

In addition to the above types, flame retardants containing chlorine and phosphorus or bromine and phosphorus are prevalent and seem to become more important as time goes by. Commercially used examples of chlorine- and phosphorus-containing flame retardants are tris(2,3-dichloropropyl) phosphate, tris(2-chloroethyl) phosphate, chlorinated polyphosphates, and bis(2-chloroethyl) vinyl phosphonate. One of the most widely used bromine- and phosphorus-containing flame retardants is tris(2,3-dibromopropyl) phosphate. It is used in fibers, foams, and certain thermoplastics. Some other examples are tris(4-bromophenyl) phosphate, tris(2,4,6-tribromophenyl) phosphate, and diethyl 2-bromoethyl phosphonate.

Flame retardants containing bromine and chlorine (for example, vinylidene chlorobromide) and bromine, chlorine, and phosphorus, for example, tris(bromochloroisopropyl) phosphate, are known but essentially not used.

Usage of Flame Retardants

The major markets for plastics can be divided into seven categories (see Table 2) (3). These seven categories accounted for 72% of all plastics used and 96% of fire-retardant polymers (4). Of the total consumption of 24.4 billion pounds of plastics in 1973, only a little more than 6% constituted fire-retarded polymers.

The largest volume end-use for fire-retarded polymers was in building and construction. Of the total of 5.2 billion pounds of plastics consumed, about 10% or 515 million pounds was classified as fire-retarded. Fire-retarded plastic growth in this segment is expected to be 13–15% per year (4).

The second largest volume end use was in the electrical and electronics industries. Fire-retarded plastics consumption amounted to 369

Table 2. Major markets for plastics—1973.

	Plastics × 10 ⁻⁶ , lb	FR plastics × 10 ⁻⁶ , lb	FR plastics %
Building and construction	5,154	515.4	10.0
Electrical/electronic	1,638	386.6	22.5
Transportation	1,551	310.2	20.0
Furnishings	1,095	164.3	15.0
Packaging	5,830	58.3	1.0
Housewares Appliances	1,363 } 938 }	23-46	1-2
Other	6,831	68	1

million pounds out of 1.6 billion pounds. Fire-retarded plastics growth is expected to be in the range of 10–12% per year range (4).

Transportation was the third largest market for fire-retarded plastics, using about 310 million pounds out of 1.6 billion pounds. This market is expected to show a major growth, as more plastics are used to produce smaller and lighter cars. Fire-retarded plastics will grow at about 17% per year in this market (4).

The next major market is in furnishings, consuming about 164 million pounds of fire-retarded plastics out of 1.1 billion pounds. Here too, a very high rate of growth (17–20%) is expected as a result of the proposed Consumer Product Safety Commission standard for upholstered furniture.

Although packaging was the largest market for plastics, only about 58 million pounds (1%) out of 5.8 billion pounds were flame-retarded. Generally, fire-retarded plastics are not required in this application.

Finally, housewares and appliances used about 2.3 billion pounds of plastics, of which only 23 to 46 million pounds (1–2%) were flame-retarded.

In summary, much activity is expected in this area as a result of tighter construction codes and stiffer government requirements for flame and smoke suppression. Better flame resistance is an increasingly pervasive legal requirement and is the prime reason for the projected overall annual growth rate of 15–17% for flame retardants.

Toxicity of Flame Retardants

Broadly speaking, all flame retardants can be subdivided into “nonreactive” and “reactive”

types. Nonreactive types are used as is prior to or during polymer processing and as a finish or surface coating. Reactive flame retardants are used as comonomers in the polymerization or grafting of the material. This leads to an important distinction as concerns the toxicity of a material when used as a flame retardant. Thus, materials to be used as nonreactive flame retardants have to be inherently nontoxic, whereas reactive flame retardants which are converted into nontoxic polymeric materials may not necessarily have to be nontoxic (vinyl chloride is an example). Of course, effective removal of traces of unreacted toxic reactive flame retardants is a problem when dealing with such materials.

Toxicological studies of flame retardants for most synthetic materials are of a rather recent origin—since late 1960's. Thus, still only a few detailed toxicological studies on flame retardants have been published. Overall we have found no evidence for persistent toxic concern from the flame retardants themselves. There is a more serious toxicological problem in the manufacturing of some flame retardants, their by-products, and possible products of degeneration. However, these problems are outside the scope of this report.

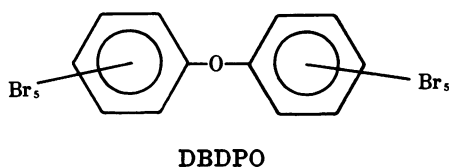
Review of Experimental Studies

Only those compositions considered commercially significant today are reviewed. Thus, we find data on 18 compounds and/or families of compounds that are pertinent. Some data on inherently flame retarded polymers are also included. The flame retardants are subdivided into the following groups: nonreactive flame

retardants, including also plasticizers which function also as flame retardants; reactive flame retardants; inorganic-nondurable flame retardants; and inherently flame-retarded polymers.

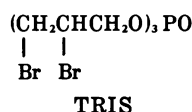
Nonreactive Flame Retardants

Decabromodiphenyl Oxide. A 2-yr toxicity study with decabromodiphenyl oxide, DBDPO (5-9) was conducted. Rats ingesting 1.0, 0.1, or 0.01 mg DBDPO/kg for 2 yr showed no discernible alterations in body weight, food consumption, hematology, organ weights, tumor formation, or tissues subjected to pathologic examination. Serum, muscle, and kidney showed no increase in bromine content. In liver,



low-level steady-state conditions were attained by 12 months. Adipose tissue showed a time- and dose-related increase in bromine content subsequent to ingestion of 1.0 or 0.1 mg DBDPO/kg-day. Despite the accumulation of bromine in adipose tissue, no discernible toxicologic effects were observed. DBDPO is neither an eye nor skin irritant nor skin sensitizer, nor is it absorbed through the skin in acutely toxic amounts; it does not possess bromacnegenic activity.

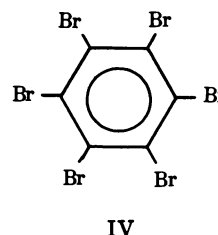
Tris(2,3-dibromopropyl) phosphate (TRIS). Acute oral LD₅₀ for TRIS (10) in male albino rats was calculated to be 5.24 g/kg. Acute dermal LD₅₀ of TRIS for male and female New Zealand white rabbits was found to be greater than 8.00 g/kg. TRIS was found not to be an eye or skin irritant in rabbits. Repeated skin patch tests on 52 human subjects showed that TRIS did not produce primary skin irritation,



skin fatigue, or skin sensitization. Rats fed 100 ppm and 1000 ppm TRIS for 28 days

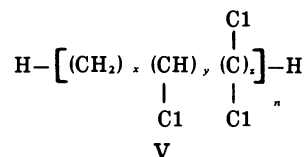
showed less weight gain and a decrease in organ weight. However, no clinical or histopathological effects were noted. Tissue residue analysis showed bromine build-up in all tissues at the end of the 28-day feed period. After 6 weeks withdrawal, residue levels decreased to essentially control levels. It is concluded that TRIS exhibits very low oral and dermal toxicity, is not a skin or eye irritant, and has a low order of subacute toxicity as determined by 28-day rat-feeding studies. A recent study (11), however, showed that 1 ppm of TRIS in water for 5 days killed goldfish (*Carassius auratus*).

Hexabromobenzene (IV) (12). Administration of hexabromobenzene to mice orally in doses from 0.875 to 7.0 g/kg-day for 30 days



had no effect on food consumption, body weight, blood serum enzymes and did not induce pathological changes in the organs examined.

Chlorinated Paraffins. Subacute toxicity tests in which as much as 1 g of chlorinated paraffin (V) per day was fed to rats for 42 days (13) produced no noticeable effects. Con-

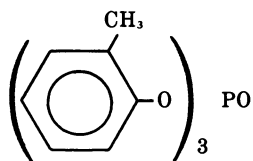


tact of the skin with chlorinated paraffins does not give rise to any irritation or sensitization.

Antimony Trioxide. Subacute oral toxicity for antimony trioxide (Sb₂O₃) administered in the food to rats for 30 days produced the following dose-symptoms relationships (14): maximum dosage having no effect, 0.27 g/kg; reduced growth, reduced appetite, micropathology in liver, kidney, spleen, or testis of any rat at 1.07 g/kg. Single dose oral LD₅₀ is higher than 20 g/kg.

Plasticizers That Also Function as Flame Retardants

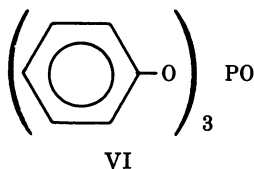
Plasticizers are mixed into polymers to increase flexibility and workability. The esters formed by reaction of the three functional groups of phosphoric acid with alcohols or phenols are excellent plasticizers. The phosphoric acid esters are also remarkable flame-retarding agents, and for this reason are extensively used in plastics. Generally, phosphoric acid esters are toxic (13). Tricresyl phosphates have been one of the most important plasticizers, and it is believed that the tricresyl phosphate used as a plasticizer is free of the *ortho* isomer.



σ -Tricresyl phosphate

The *ortho* isomer has prominent neurotoxic properties. The question of the purity of materials in this group because of the neurotoxic components is a very serious one.

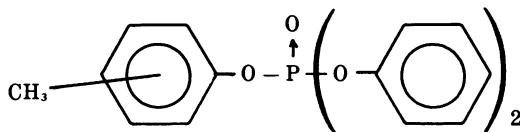
Triphenyl Phosphate. Repeated ingestion by rabbits of doses of triphenyl phosphate (VI) varying between 0.10 g and 1 g/kg body weight gave rise to kidney damage (13, 15) which,



VI

however, cleared up. Intraperitoneal injections of 0.1–0.2 g/kg do not have any toxic effect. Subcutaneous injection of 1 g/kg was fatal to rabbits.

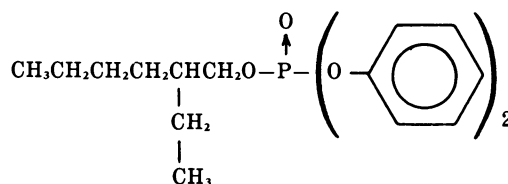
Cresyl Diphenyl Phosphate. Intraperitoneal doses of cresyl diphenyl phosphate (VII) over



VII

1 g/kg body weight are fatal to rats. Oral doses up to 4 g/kg have been tolerated (13, 16). The material possesses moderate skin irritant action in rabbit and man.

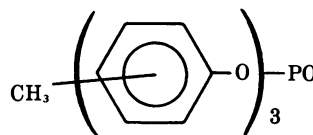
2-Ethylhexyl Diphenyl Phosphate (Santizer 141). Rats were kept for at least 2 yrs on diets containing 5.0, 1.0, 0.125, and 0.0625% ethylhexyldiphenyl phosphate (VIII). The diets containing 0.125 and 0.0625% of the phosphate had no adverse effects (13, 17). Dogs were fed on diets containing 2.5 and 1.5% of the phosphate for 6 days a week over 2 years.



VIII

Dogs experienced normal weight gain, and nothing in particular was found at macroscopic or microscopic post-mortem examinations. In rabbits single doses up to 24 g/kg have not caused death. To sum up, the substance has a low toxicity and its use in contact with food has been authorized by the Food and Drug Administration.

Tricresyl Phosphate. Tricresyl phosphate (IX) is claimed to be the most toxic of all plasticizers in general use (13). In rabbits, a single dose of 0.10 g/kg is fatal; in dogs the dose is 0.50 g/kg (13, 15). In white mice, a single dose of 12 mg/g is fatal when injected subcutaneously. The minimum toxic dose for human beings has not been stated precisely. In general, it is very low, and traces are enough

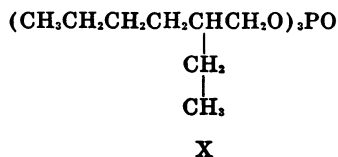


IX

to cause paralysis of the extremities of the limbs. Of the three positional isomers, the *meta* isomer is less toxic and the *para* isomer is very slightly toxic. Of the mono-, di-, or tri-*o*-cresyl esters, the monoester in animals was six times more toxic than the tri-*o*-cresyl ester.

Tri-2-ethylhexyl Phosphate. Tri-2-ethylhexyl phosphate (X) has only a very slight

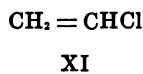
acute toxicity; for rats the lethal dose LD₅₀ is 39.8 g/kg. Subacute oral toxicity for the



phosphate given in the food to rats for 30 days produced the following dose-symptoms relationship: maximum dose having no effect, 0.43 g/kg, reduced growth at 1.55 g/kg.

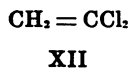
Reactive Flame Retardants

Vinyl Chloride. There is probably more toxicological information now on vinyl chloride (XI) than any other monomer (13, 18-22). For example, a recent paper on health effects of vinyl chloride monomer contains an annotated bibliography of some 162 references (19). The monomer, but not the polymer, is toxic and is a carcinogen. When rats were exposed



to 50 to 10,000 ppm of atmospheric concentrations of vinyl chloride, 4 hr/day, 5 days/week for 12 months, angiosarcomas, symbl gland carcinomas, and nephroblastomas were developed. The upper exposure limit of 1 ppm averaged over an 8-hr period has been set by the Occupational Safety and Health Administration of the Department of Labor.

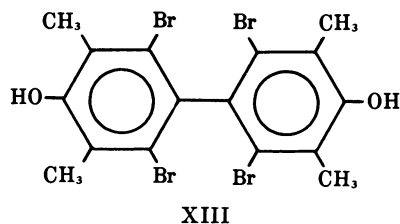
Vinylidene Chloride. Exposure of rats to 500 ppm of vinylidene chloride (XII) for 6 hrs caused nose irritation, retarded weight gain, and liver cell degeneration (13, 18, 23).



For a 4-hr exposure, the lethal dose LD₅₀ for rats was found to be of the order of 32,000 ppm.

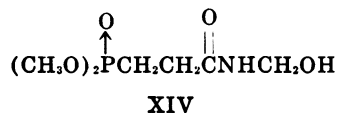
2,2',6,6'-Tetrabromo-3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl (TTDB). Acute toxicity studies in rabbits and rats showed that TTDB (XIII) is a possible eye irritant, (is not a primary skin irritant, and is not a toxic material by the dermal route of administration and by

the oral route of administration (24). A lethal dose of LD₅₀ of 5 g/kg was observed. In a 28-day chronic toxicity studies, rats were fed TTDB at dosage levels of 1, 10, 100, and



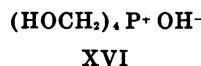
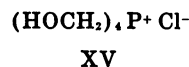
1000 ppm. No changes considered to be related to TTDB were seen in behavior, appearance, body weight, food consumption, gross or microscopic pathologic lesions, or organ weight variations.

N-Methylol dimethylphosphonopropionamide (Pyrovatex FR). Pyrovatex (XIV) shows

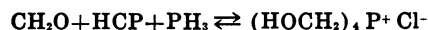


only a very slight acute toxicity when administered orally to rats (25). A lethal dose LD₅₀ of 6 g/kg was observed. It produces no perceptible signs of skin irritation.

Tetrakis(hydroxymethyl)phosphonium chloride and Hydroxide. THPCl (XV),



THPOH (XVI), and Pyrovatex FR are practically the only flame retardants currently used for cotton textiles (26). THPCl is a water-soluble compound prepared from formaldehyde, phosphine, and hydrogen chloride. The



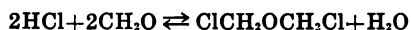
THPCl, THPOH flame-retardant system is an extremely versatile one as can be seen from some of the variations used: THPCl + methylolmelamine + urea; THPCl + methylolmelamine + urea + NH₃; THPCl + NaOH + NH₃;

THPCl + NaOH + NH₃ + amide; THPCl + NaOH + methylomelamine + urea; THPCl + NaOH + methylolmelamine + urea + copper salt. The final flame-retardant composition on the fabric can be broadly characterized as a highly crosslinked, aminated, phosphine oxide one. The THPCl reacts with the amine groups in the system, and following hydrolysis loses chlorine, resulting in the general composition XVII.



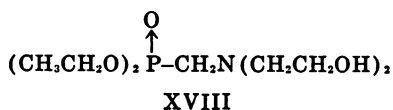
XVII

During the curing of the composition on the fabric, HCl and formaldehyde are generated. To eliminate the problem of HCl generation, sodium hydroxide can be used in the formulation. Heat and moisture have been shown to degrade the THPCl or THPOH finishes. It has been shown experimentally that detectable amounts of formaldehyde, hydrogen chloride, and phosphine are given off for as long as 2 months after the finishing operation (27, 28). The danger here is that sufficient amounts of formaldehyde and hydrogen chloride could conceivably be given off to generate spontaneously small amount of bis(chloromethyl) ether (29).



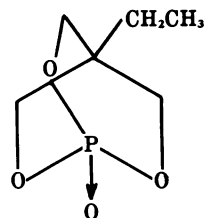
In the study by Afanazeva et al. (27), it was shown that six THPCl formulations produced local irritant and systemic effects. Topical applications of aqueous extracts resulted in death of up to 70% of the experimental mice. However, the dosages used were not given and the presence of bis(chloromethyl) ether was not demonstrated. Recently it was shown that 1 ppm of THPOH in water for 5 days was toxic to goldfish (*Carassius auratus*) (11). Furthermore, THPCl was found to be one of the most intense skin irritants tested (30).

O,O-Diethyl-N,N-bis (2-hydroxyethyl) aminomethyl Phosphonate. O,O-Diethyl-N,N-bis (2-



hydroxyethyl) aminomethyl phosphonate (XVIII) is presumably a nontoxic flame retardant, but

when used in a polyurethane foam formulation during the combustion of the foam decomposes and is known to be (31, 32) responsible in part for the generation of an extremely toxic combustion product, 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane-1 oxide (XIX). This apparently can occur when polyols based on other than trimethylol propane are also used.



XIX

The reported LD₅₀ for XIX, when administered interperitoneally to mice, is 1 mg/kg (33). This represents a relative toxicity level of approximately six times that for diisopropyl-fluorophosphate (a chemical warfare agent) or parathion (an insecticide).

Inorganic Nondurable Flame Retardants

The use of nondurable flame retardants has been declining since about late 1950's and their usage in plastics has been minor. The major markets are in paper and wood products and forest fire fighting. Some of the more common formulations consist of the following: borax/boric acid mixtures, Na₂B₄O₇ · 10H₂O/H₃BO₃; ammonium sulfamate, NH₄SONH₂; diammonium phosphate, (NH₄)₂HPO₄; ammonium bromide, NH₄Br. The borax/boric acid compositions appear to be the least toxic of all the nondurables. Ammonium sulfamate is sold also as a weed killer and reportedly has an oral LD₅₀ in rats of 3.9 g/kg. Ammonium phosphates can cause skin irritation; however, one of their long-term usages has been in fertilizers. Ammonium bromide is a sedative at oral doses of 0.6-2 g.

Inherently Flame-Retarded Polymers

In general, most synthetic high polymers are chemically inert and exhibit only slight or no physiological and toxicological effects. However, there are distinct differences in their action depending upon the mode of their introduction into the body.

Some of the polymers with inherent flame-retardant properties which have been investigated for their toxicological properties are: poly(vinyl chloride), vinyl chloride/vinylidene chloride copolymer, polytetrafluoroethylene, and chlorinated rubber.

Poly(vinyl chloride) tubes as a prosthetic material for replacing the esophagus of a dog gave rise to no irritation and were very well tolerated by the animal (34).

Vinyl chloride/vinylidene chloride copolymer has been incorporated (5%) in a daily diet for dogs and rats (35). The dogs were maintained on the diet for 1 year and the rats for 2 years, and no signs of poisoning were found in these animals.

Polytetrafluoroethylene has been evaluated in rats. Feeding a diet containing 25% of finely powdered polytetrafluoroethylene induced no symptoms of poisoning (36).

Subacute oral toxicity tests on rats with "chlorinated rubber" indicated the material to be as innocuous as the chlorinated paraffins were (13).

Conclusion

In general, flame retardants *per se* present less problems than the components from which they are manufactured, by-products in their manufacture, and products of their degradation. More studies on their toxicity and of the decomposition products of flame retardants when they reside in the polymer substrates are badly needed.

Another emerging area that needs more attention is the area of multiple-functional additives. The matter of combining in a single product the additive functions that formerly required two or three or more separate materials is a cost-efficient trend that will become more important. We already are familiar with one such group of materials, the phosphate plasticizer-flame retardant materials. Incidentally, this group of materials, because of the possibility of the presence of neurotoxic components, needs a lot more toxicological evaluation work than appears to be available.

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